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Computationally Based Measures of Amine Azide Basicity and Their Correlation With Hypergolic Ignition Delays

by Michael J. McQuaid

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14. ABSTRACT

To explore a hypothesis that hypergolic ignition delays for fuel-nitric acid combinations are a function of the fuel's basicity, measures of base strength are computed for various azides, amines, amine azides, and hydrazines and compared to ignition delay data. Measures of base strength considered include gas-phase proton affinities, heats of neutralization for reactions leading to ion pairs, and heats of reaction for fuel-nitric acid complexation. The measures quantify substituent-mediated basicity differences between sites with lone pair electrons, but they do not appear to be good predictors of ignition delay. The failure of the hypothesis is discussed.

15. SUBJECT TERMS

computational chemistry, hypergolic ignition delay, base strength

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1. Introduction

Storable hypergolic liquid (or gel) fuel-oxidizer combinations (i.e., those that react spontaneously upon mixing) provide an extremely reliable basis on which to design intermittent and/or variable thrust rocket propulsion systems. As such, they are expected to propel beyond line-of-sight weapons carried by the U.S. Army's Future Combat System, an example being the loitering attack missile being developed under the NetFires technology demonstration program. Unfortunately, the best performing propellant combinations developed to date have fuels derived from hydrazine, monomethylhydrazine (MMH), and/or unsymmetrical dimethylhydrazine (UDMH)—all of which are acutely toxic and suspected carcinogens. Thus, their utilization requires the implementation of burdensome and costly handling procedures.

Searching for alternatives to hydrazine-based fuels, the U.S. Army, led by the U.S. Army Aviation and Missile Research, Development, and Engineering Center (AMRDEC), has found that 2-azido-N,N-dimethylethanamine (DMAZ) performs competitively with Aerozine-50 (a 50/50 mixture of hydrazine and UDMH) in inhibited red fuming nitric acid (IRFNA) oxidized experimental systems (*1, 2*). DMAZ has also been found to be less toxic than hydrazine-based fuels. DMAZ-IRFNA systems do not, however, meet "ignition delay" standards set by MMH-IRFNA systems, which, negatively impacting engine design, may preclude DMAZ's fielding.

To address the ignition delay issue, 2-azidoethanamines with substituents other than the two methyl groups in DMAZ have been synthesized and tested. Trial and error testing of a class of compounds related to a promising candidate is a traditional approach to fuel development, and it was employed in developing the fuel-oxidizer combinations that are fielded in hypergolic propulsion systems today. Clark provides an excellent history of the era that led to those combinations (*3*). Involving the testing of hundreds of different amines, hydrazines, and alcohols during the 1950s, accessible data on these systems are, however, sparse because at that time the best combinations were classified or held proprietary.

With the establishment of hydrazines as fuels of choice in the mid-1950s, some of the work on discarded candidates began to appear in the open literature, with the issue of ignition delay the subject of several papers. Relevant to (the amine) DMAZ were experimental studies by Rapp and Strier (*4*) and (separately) Schalla and Fletcher (*5, 6*). Both groups discuss the differences in ignition delay found for a wide variety of amines when they were oxidized by (nominally) white fuming nitric acid (WFNA). Rapp and Strier (*4*) suggest that the ignition delays for amines correlate with whether the amine is primary (R-NH_2), secondary (R_2-NH), or tertiary (R_3-N), ignition delays decreasing in that order, and (by inference) with base strength. Schalla and Fletcher (*5, 6*) also recognize the importance of (acid-base) neutralization, but, finding ignition delays sensitive to oxidizer/fuel (O/F) ratios, propose that the best combinations will be those for which the ratios, (1) optimal for combustion and (2) optimal for neutralization, are nearly the

same. In the absence of an amine or other strong reducing group, compounds with azide groups are very weak bases and are not hypergolic.

Given that alkyl amines have long ignition delays and that alkyl azides are not hypergolic, the relatively short ignition delays of DMAZ and some other amine azides are surprising. Moreover, there are performance differences between fuels in this class of compounds that are at odds with the expectation that shorter ignition delays will be found for compounds that are stronger bases. For example, a typical measure of a compound's base strength, namely *aqueous* pK_a,

$$pK_a = -log \frac{[B][H_3O^+]}{[BH^+]},$$ (1)

which describes the equilibrium of the system

$$BH^+ + H_2O \ll B + H_3O^+,$$ (2)

expresses the base strength of B in terms of the acid strength of the ion BH^+, a higher pK_a indicating a higher base strength. As such, this measure would predict that 2-azido-N-methylethanamine (MMAZ, $pK_a = 9.3$) (*1*), which has one methyl group in lieu of the two in DMAZ, would ignite faster than DMAZ ($pK_a = 8.5$) (*1*). But MMAZ has not been observed to be hypergolic.

In considering this contradiction with expectations, it was noted that the ignition delays of dimethylamine ($pK_a = 10.9$) (*7*) and trimethylamine ($pK_a = 9.8$) (*7*) also fail to correlate with their pK_as. And a comparison of pK_as would suggest that the simple alkyl amines would have shorter ignition delays than their corresponding amine azides. Given the trend from ammonia ($pK_a = 9.25$), to methylamine ($pK_a = 9.8$), to dimethylamine ($pK_a = 10.9$) (*7*), the pK_as of trimethylamine (relative to dimethylamine) and DMAZ (relative to MMAZ) are surprising. (In the case of trimethylamine, the observation has been attributed to steric effects that oppose protonation [*7*].) But the gas–phase proton affinities (*PA*s) of these compounds, i.e., the exothermicity of proton attachment to the fuel,

$$B + H^+ \circledR BH^+,$$ (3)
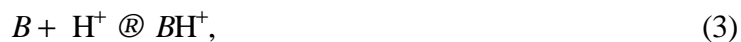
which are a site-specific measure of base strength, do, for this limited series, correlate with ignition delays. Coupled with the fact that the reaction of interest is

$$B + HA \circledR BH^+ + A^-$$ (4)
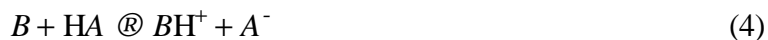
in a bath of B and the acid HA, the dielectric constant of which is likely to be lower than that of water, the deficiency of aqueous pK_a as a predictor of ignition delay can be rationalized. However, since (neat) hypergolic fuels (by definition) react violently with acids, experimental determinations of reaction (4) equilibria are problematic. Moreover, any experimental measure requires a development step that one hopes to avoid, i.e., the synthesis and testing of a compound that is not going to perform well.

Bespeaking the need for computationally based estimates of reaction (*4*) exothermicites (re: heats of neutralization), a density functional theory-based model was employed to estimate them for a variety of fuels whose ignition delays have been experimentally measured. For modeling the influence of the solvating medium, a polarizable continuum model (PCM) was employed. As will be discussed, the results obtained suggest deficiencies in the approach/model. Therefore, other measures of fuel base strength were sought, and various gas-phase measures were calculated. They include (1) heat of neutralization for ion pair formation resulting from nitric acid reacting with a fuel cluster, (2) proton affinity (*PA*), and (3) the exothermicity of fuel-nitric acid complexation. Selected results are presented, and their correlation with ignition delay is evaluated based on the (qualitative) rankings of fuel ignition delays given in figure 1. These rankings, which were established from the highly test-dependent absolute values reported by Rapp and Strier (*4*), Schalla and Fletcher (*5, 6*), Stevenson (*1*), and Thompson et al. (*2*), assume that orderings are test independent.

Different Families

Hydrazines < Amine Azides < Alkyl Amines < Azides

Same Family

— Hydrazines

$$MMH < N_2H_4$$
$$MMH \leq UDMH$$

— Alkyl Amines

Tertiary < Secondary < Primary < Ammonia

— Amine Azides

CPAZ $\leq$ DMAZ < MORPHAZ < MMAZ
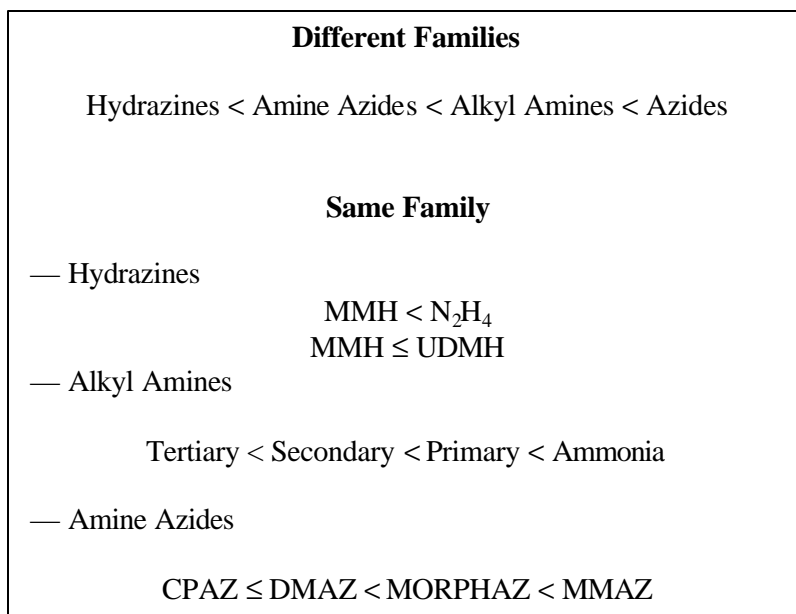
Figure 1. Ignition delay ordering derived from experimental testing.

2. Theoretical Methods

The Gaussian 98 (G98) suite of quantum chemistry (QM) codes was employed to identify equilibrium molecular structures and obtain their zero point corrected energies (ZPE) (*8*). Hydrogen bonding and proton transfer to fuel sites with lone pair electrons were the only interactions considered. (Figure 2 shows such sites for representative molecules.) The choice of model—DFT using the B3LYP exchange-correlation functionals and a 6-311++G(d,p) atomic
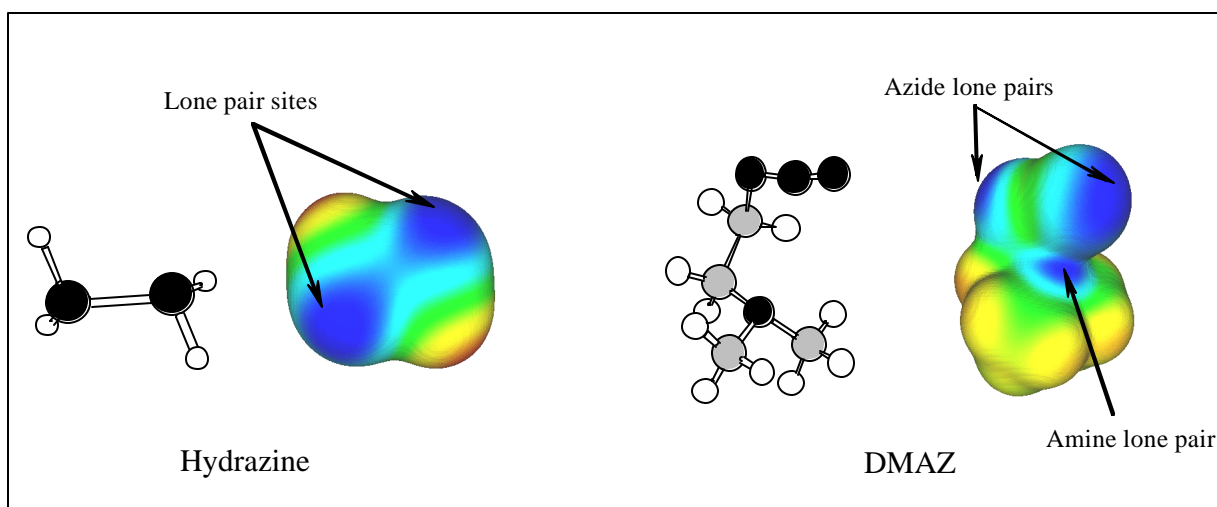
Figure 2. Electrostatic potentials on electronic isodensity surfaces for DMAZ and hydrazine. Dark gray regions correspond to sites with lone pair electrons.

orbital basis set on a G98-defined "ultrafine" grid—was based on the success achieved with it in characterizing DMAZ (*9*). Following the work of Tao and coworkers (*10*), who studied ammonia-nitric acid proton transfer reactions mediated by water, use of the self-consistent isodensity PCM (SCI-PCM) for simulating solvent effects was attempted. However, after encountering difficulties in applying the method, it was learned that Gaussian Incorporated's attempt to upgrade the model from the G92 version used by Tao had rendered it unusable. Therefore, based on a recommendation (*11*), the polarizable conductor PCM (CPCM) (*12*) was employed to obtain optimized structures, and it was employed to obtain energies as well. Unfortunately, the method appears to produce anomalous results (that are to be discussed), and attempts to address concerns by employing (1) finer grids and (2) more tesserae to define the solute cavity did not resolve them. Thus, the focus of the study was shifted to characterizing the energetics of gas-phase reactions, a second study by Tao (*13*), this time on HNO_3-NH_3-$(H_2O)_x$ systems, guiding the effort.

3.   Results

3.1   Solvated Reactions via a Polarizable Continuum Model

Figure 3 shows the $\boldsymbol{DH_r(0)}$ dependence on dielectric constant ($\boldsymbol{e}$) for reactions,

$$B + HNO_3 \ \circledR \ BH^+ + NO_3{}^-, \tag{5}$$

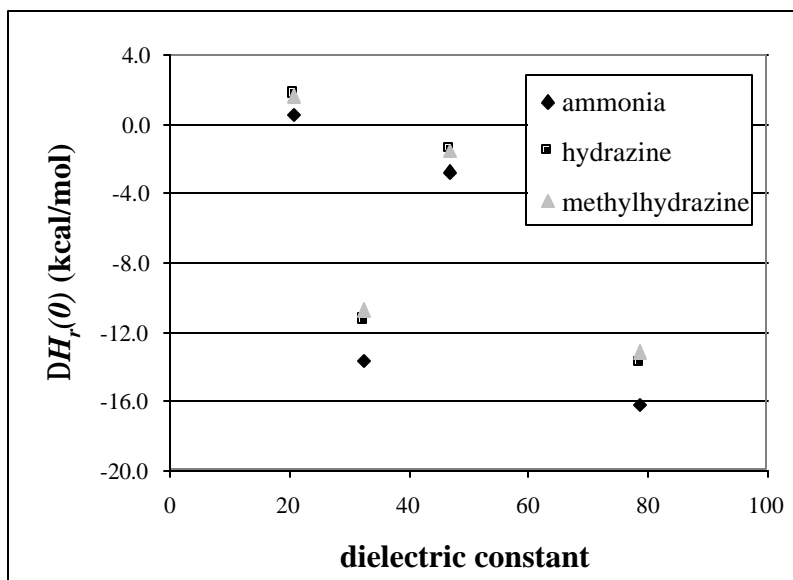where B is ammonia, hydrazine, or MMH. At -16.5 kcal/mol, the computed exothermicity of

Figure 3. $\Delta H_r(0)$ for $B + HNO_3 \circledR BH^+ + NO_3^-$ as a function of dielectric constant, B being ammonia, hydrazine, or MMH.

ammonia's neutralization by nitric acid in water ($e = 78$) is in line with the value for its neutralization by HF in water (-15.2 kcal/mol) (*13*). For the neutralizations of hydrazine and MMH (in which case it is assumed that the proton transfers to the methylated nitrogen), the exothermicities are observed to be nearly identical to each other and less than ammonia. Also comparable to the values for these compounds when they are neutralized by HF (*13*), the values are again considered reasonable. However, for dielectric constants in the range that HNO₃ ($\varepsilon =$ 50 ± 10) (*14*), hydrazine ($e = 52$) (*15*), MMH ($e = 19$) (*15*), and ammonia ($e = 17$) (*16*) fall, the results are contrary to expectations. First, as the dielectric constant decreases, electrostatic effects become more important and it is expected that the $\Delta H_r(0)$ will *steadily* increase, not zigzag up, to its gas-phase value. In addition it is expected that these reactions will still be exothermic in a medium whose dielectric constant ($e = 21$, the value for acetone [*16*]) is slightly higher than that of MMH. Given the suspected unreliability of the method and the fact that the dielectric constant appropriate to use for the comparison would be uncertain, no attempt was made to apply it to amine azides.

3.2 Gas-Phase Cluster Reactions

Unable to rely on the PCM results for estimating a compound's heat of neutralization per reaction (5), the possibility of estimating this property via gas-phase reactions involving fuel molecule clusters (B_x),

$$B_x + HNO_3 \circledR (BH^+)B_{x-1} + NO_3^-, \tag{6}$$
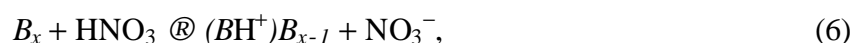
was investigated. As a check of the reliability of the theoretical model for calculating the energetics of such reactions, *PA*s and exothermicities for ion cluster reactions,

5

$$B + (BH^+)B_{x-1} \circledR (BH^+)B_x, \tag{7}$$

were obtained for systems for whom these values have been experimentally determined. Table 1 shows the PAs determined for ammonia, methylamine, dimethylamine, and trimethylamine, their values being ~2 kcal/mol less than values recommended by Hunter and Lias (*17*). The calculated PA of NO_3^- is also less than the most recently reported experimental value (identified via the National Institute of Standards and Technology [NIST] Chemistry WebBook [*18*]). Thus, a slight systematic error in the model results is indicated. However, it is considered that the results are still useful as a relative measure of base strength, and gas-phase heats of neutralization calculated from the values, i.e.,

$$\mathit{DH_r(0)} = PA(HNO_3) - PA(B_x), \tag{8}$$

should be reasonably accurate because the errors cancel. Table 2 compares calculated $\mathit{DH_r(0)}$ values for ammonia cluster reactions, the agreement with experimentally obtained values[*] again being reasonable.

Table 1. PAs as calculated via B3LYP/6-311++G(d, p) and their comparison with recommended values.

Compound	ZPE (Hartrees)		PA (kcal/mol)		
	B	BH^+	Calc.	Exp.	Diff
NH_3	−56.548462	−56.870875	202.3	204.0	−1.7
CH_3NH_2	−95.830097	−96.169918	213.2	214.9	−1.8
$(CH_3)_2NH$	−135.117679	−135.468575	220.2	222.2	−2.0
$(CH_3)_3N$	−174.408125	−174.765789	224.4	226.8	−2.4
NO_3^-	−280.443771	−280.952367	319.1	324.5	−5.4

Table 2. $\mathit{DH_r}$ for $B+(BH^+)(B)_x \circledR (BH^+)(B)_{x+1}$ reactions as calculated via B3LYP/6−311++G(d, p) and their comparison with experiment.

$(RH^+)(R)_x$	ZPE (Hartrees)			DH_r (kcal/mol)	
	B	$(BH^+)(B)_x$	$(BH^+)(B)_{x+1}$	Calc.	Exp.
NH_4^+	−56.548462	−56.870875	−113.462147	26.9	21±10
$(NH_4^+)(NH_3)$	−56.548462	−113.462147	−170.038614	17.6	13±10
$(NH_4^+)(NH_3)_2$	−56.548462	−170.038614	−226.609823	14.3	14±6
$(NH_4^+)(NH_3)_3$	−56.548462	−226.609823	−283.176876	11.7	12±6
$(CH_3)_3NH^+$	−174.408125	−174.765789	−349.204815	19.4	22±6

The theoretical model so validated, reaction (6) $\mathit{DH_r(0)}$ values for various ammonia and hydrazine clusters were computed with it. Shown in figure 4, the results indicate that even for an $(NH_3)_5 + HNO_3$ reaction, the process is endothermic. (As will be discussed in section 3.4,

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[*]The experimental values reported are from a search of the NIST Chemistry WebBook that was checked in March 2003. The values are the average of data from up to nine different studies.
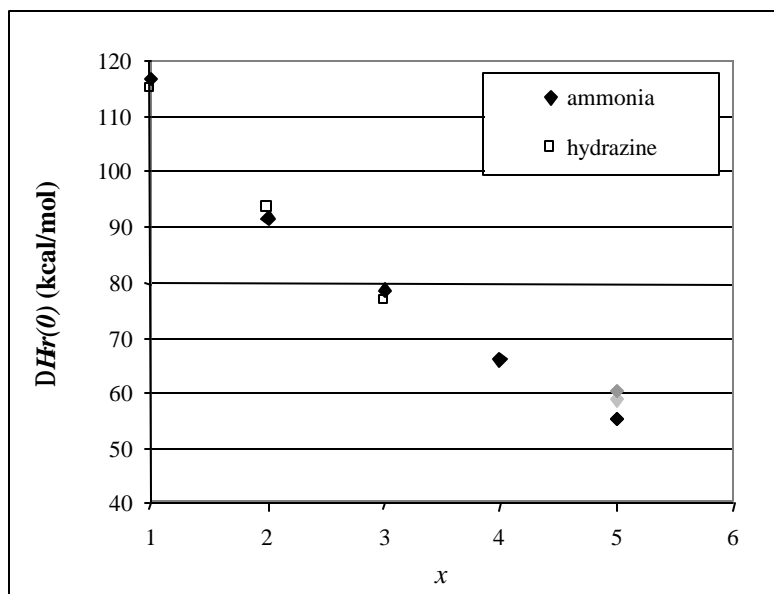
Figure 4. $DH_r(0)$ for $B_x + HNO_3 \rightarrow (BH^+)B_{x-1} + NO_3^-$, where B is ammonia or hydrazine.

on the basis of bond lengths, a proton will transfer from nitric acid to ammonia when their interaction is mediated by just two other ammonia molecules.) Demonstrating that larger $B_x/(BH^+)B_{x-1}$ clusters and/or $(B_y)HNO_3/B_yNO_3^-$ clusters would have to be characterized in order to approximate the energetics of condensed-phase proton transfer reactions, the results indicated that such studies would not be feasible (within program resources) for amine azides. Therefore, the effort was terminated.

3.3 Gas-Phase *PA*s

Beyond a validation exercise, the table 1 results, which are shown graphically in figure 5, are interesting because the trend in base strength expected for the series ammonia, methyl amine, dimethylamine and trimethylamine is in fact observed in this gas-phase measure and, as opposed to pK_a, correlate with ignition delay rankings reported for the set. Therefore, it was decided to simply compute the gas-phase *PA*s of various fuels in the hope that they might provide some insight or predictive capability. Tables 3, 4, and 5 present the results for selected azides, amine azides, and hydrazines, respectively.

As shown in table 3, the two lone pair sites associated with the azide group have significantly different *PA*s, the *PA* of the site associated with N_a (for a generically labeled azide R-N_a-N_b-N_c) ranging from 11–20 kcal/mol higher than the *PA* of N_c. The *PA*s of both azide sites are also observed to be considerably lower than those of the amines or hydrazines, which, given the nonhypergolic nature of alkyl azides, is consistent with the hypothesized correlation between basicity and ignition delay.
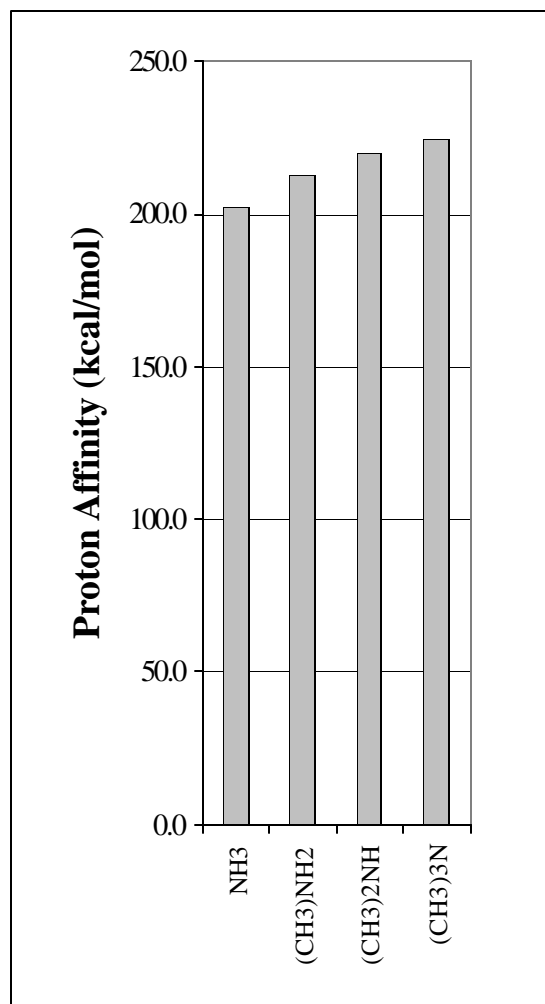
Figure 5. B3LYP/6-311++G(d,p) calculated *PA*s
for alkylamines.

Table 3. B3LYP/6-311++G(d,p) calculated *PA*s for azides.

	ZPE (Hartrees)		*PA* (kcal/mol)
	B	*B*H$^+$	
Azide N$_a$			
hydrazoic acid	−164.814684	−165.096042	176.6
methylazide	−204.103331	−204.402324	187.6
gauche-ethylazide	−243.402659	−243.707492	191.3
anti-ethylazide	−243.403173	−243.707329	190.9
cyclopropylazide	−281.472790	−281.779361	192.4
Azide N$_c$			
hydrazoic acid	−164.814684	−165.064259	156.6
methylazide	−204.103331	−204.378959	173.0
gauche-ethylazide	−243.402659	−243.684641	176.9
anti-ethylazide	−243.403173	−243.684643	176.6
cyclopropylazide	−281.472790	−281.761122	180.9

Table 4. B3LYP/6-311++G(d, p) calculated *PA*s for amine azides.

| | ZPE (Hartrees) | | *PA* (kcal/mol) |
	B	*B*H⁺	
Amine **N**			
MMAZ_B	−338.036614	−338.391753	222.9
MMAZ_D	−338.038432	−338.391758	221.7
CPAZ_B	−415.408210	−415.763606	223.0
CPAZ_D	−415.409896	−415.763057	221.6
MORPHAZ_B	−529.956689	−530.316497	225.8
MORPHAZ_D	−529.955307	−530.316508	226.7
DMAZ_B	−377.325354	−377.686803	226.8
DMAZ_D	−377.323743	−377.686788	227.8
DMAZ_E	−377.324671	−377.675547	220.2
cis-ADMCPA_A	−415.399113	−415.759059	225.9
cis-ADMCPA_B	−415.397585	−415.759061	226.8
trans-ADMCPA_A	−415.401984	−415.751610	219.4
trans-ADMCPA_B	−415.401658	−415.750070	218.6
Azide **N_a**			
MMAZ_B	−338.036614	−338.355892	200.3
MMAZ_D	−338.038432	−338.354366	198.3
CPAZ_B	−415.408210	−415.724676	198.6
CPAZ_D	−415.409896	−415.724265	197.3
MORPHAZ_B	−529.956689	−530.272798	198.4
MORPHAZ_D	−529.955307	−530.273465	199.6
DMAZ_B	−377.325354	−377.649957	203.7
DMAZ_D	−377.323743	−377.649952	204.7
cis-ADMCPA_A	−415.399113	−415.722159	202.7
cis-ADMCPA_B	−415.397585	−415.721171	203.1
trans-ADMCPA_A	−415.401984	−415.712909	195.1
trans-ADMCPA_B	−415.401658	−415.711713	194.6
Azide **N_c**			
MMAZ_B	−338.036614	−338.337588	188.9
MMAZ_D	−338.038432	−338.334267	185.6
CPAZ_B	−415.408210	−415.704070	185.7
CPAZ_D	−415.409896	−415.707896	187.0
MORPHAZ_B	−529.956689	−530.255856	187.7
MORPHAZ_D	−529.955307	−530.253360	187.0
DMAZ_B	−377.325354	−377.631078	191.8
DMAZ_D	−377.323743	−377.628630	191.3
cis-ADMCPA_A	−415.399113	−415.770410	233.0
cis-ADMCPA_B	-415.397585	−415.770397	233.9
trans-ADMCPA_A	−415.401984	−415.769915	230.9
trans-ADMCPA_B	−415.401658	−415.769935	231.1

Table 5. B3LYP/6-311++G(d,p) calculated *PA*s for hydrazines.

	ZPE (Hartrees)		*PA* (kcal/mol)
	B	*B*H$^+$	
Unmethylated **N**			
N$_2$H$_4$	−111.857403	−112.182796	204.2
MMH	−151.148318	−151.480130	208.2
UDMH	−190.439913	−190.777564	211.9
Methylated **N**			
MMH	−151.148318	−151.486580	212.3
SDMH	−190.464929	−190.810947	217.1
UDMH	−190.439913	−190.787748	218.3

Selected from a larger set of 2-azidoethanamines whose *PA*s were calculated, the choice of compounds included in table 4 deserves comment. As two ends of the ignition delay spectrum observed in the 2-azidoethanamines synthesized and tested by AMRDEC, the *PA*s of MMAZ and DMAZ are obviously of interest. The results for 2-azido-N-cyclopropanamine (CPAZ), which based on AMRDEC testing has an ignition delay similar to DMAZ, are considered instructive because CPAZ's stoichiometry ($C_5H_{10}N_4$) is similar to that of DMAZ ($C_4H_{10}N_4$), but as a secondary amine, it is similar to MMAZ ($C_3H_8N_4$). To include a comparison with a second tertiary amine azide, results for 4-(2-azidoethyl)morpholine (MORPHAZ) are presented. Reported to be "weakly hypergolic"(*1*), its ignition delay is assumed to be longer than DMAZ and shorter than MMAZ's. The *cis* and *trans* forms of 2-azido-N,N-dimethylcyclopropanamine (ADMCPA) are notional molecules designed to promote and prevent, respectively, the shielding of the amine lone pair electrons by the azide group (*19*).

The conformers listed in the table were selected from a larger set generated in the course of searching for geometry-dependent differences in each compound. Those chosen are considered representative of the larger group. Conformer details can be found elsewhere (*9, 19, 20*). For MMAZ, CPAZ, MORPHAZ, and DMAZ, the designations B and D define a nominal configuration of the -CH$_2$-CH$_2$-N$_3$ chain. Those definitions are the same for each molecule, and are consistent with a previous publication (*9*). Figure 6 depicts them for the case of DMAZ. Conformer B is DMAZ's lowest energy structure (*9*). Conformer D analogs are the lowest energy conformers found for MMAZ and CPAZ (*20*). Conformer E is the 2-azidoethanamine structure most analogous to the *cis* and *trans* isomers of ADMCPA. ADMCPA conformers A and B are the two lowest energy structures of these molecules. (The A conformers are shown in figure 7.) In the case of *cis*-ADMCPA, conformer A is ~1 kcal/mol lower in energy than conformer B (*21*). In the case of *trans*-ADMCPA, the energies of A and B are nearly identical.

Selected results from table 4 are presented graphically in figure 8. The *PA*s calculated for the secondary amines in MMAZ and CPAZ (222–223 kcal/mol) and the tertiary amines in
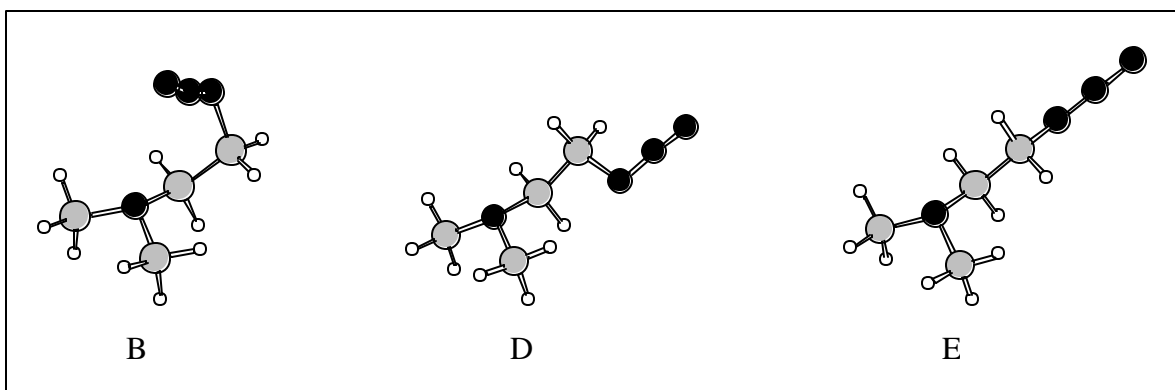
Figure 6. DMAZ conformers B, D, and E. Black circles denote nitrogen, gray circles denote carbon, and white circles denote hydrogen.
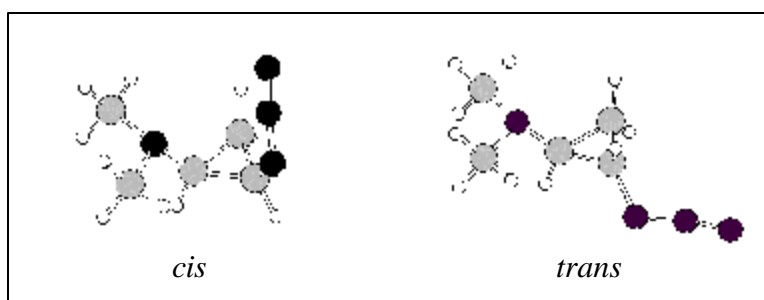

Figure 7. ADMCPA isomers. Black circles denote nitrogen, gray circles denote carbon, and white circles denote hydrogen.

MORPHAZ and DMAZ (226–227 kcal mol) are nearly identical to those for dimethylamine (222 kcal/mol) and trimethylamine (227 kcal/mol), respectively. And as in the case of the alkyl amines, the ignition delays of MMAZ and DMAZ correlate with this measure. However, the nearly identical *PA*s for the amine sites in (1) hypergolic CPAZ and nonhypergolic MMAZ, and (2) weakly hypergolic MORPHAZ and hypergolic DMAZ, deny a strong correlation between the *PA* of the amine site and ignition delay in 2-azidoethanamines.

The results for the ADMCPA isomers are somewhat surprising. It was expected that, as tertiary amines with one substituent being a cyclopropyl group, their *PA*s would meet or exceed those of DMAZ. But the *PA*s of the *cis*-ADMCPA conformers are slightly lower than DMAZ_B and DMAZ_D *PA*s, and the *PA*s of the *trans*-ADMCPA isomers are even lower than MMAZ_B and MMAZ_D *PA*s. The results for the *PA* of DMAZ_E, however, appear able to reconcile the disagreement with expectations. The *PA* of DMAZ_E is less than the *PA*s for MMAZ_B and MMAZ_D, but this is a spurious result. Based on simply using the energy of the BH$^+$ structure resulting from a geometry optimization started with a configuration in which a proton has been attached to the neutral conformer, the protonated structure is a strained configuration that is not representative of the end state of the reaction. Thus the result can be discounted. Given that the ADMCPA isomers are most closely analogous to DMAZ conformer E, it is possible that the
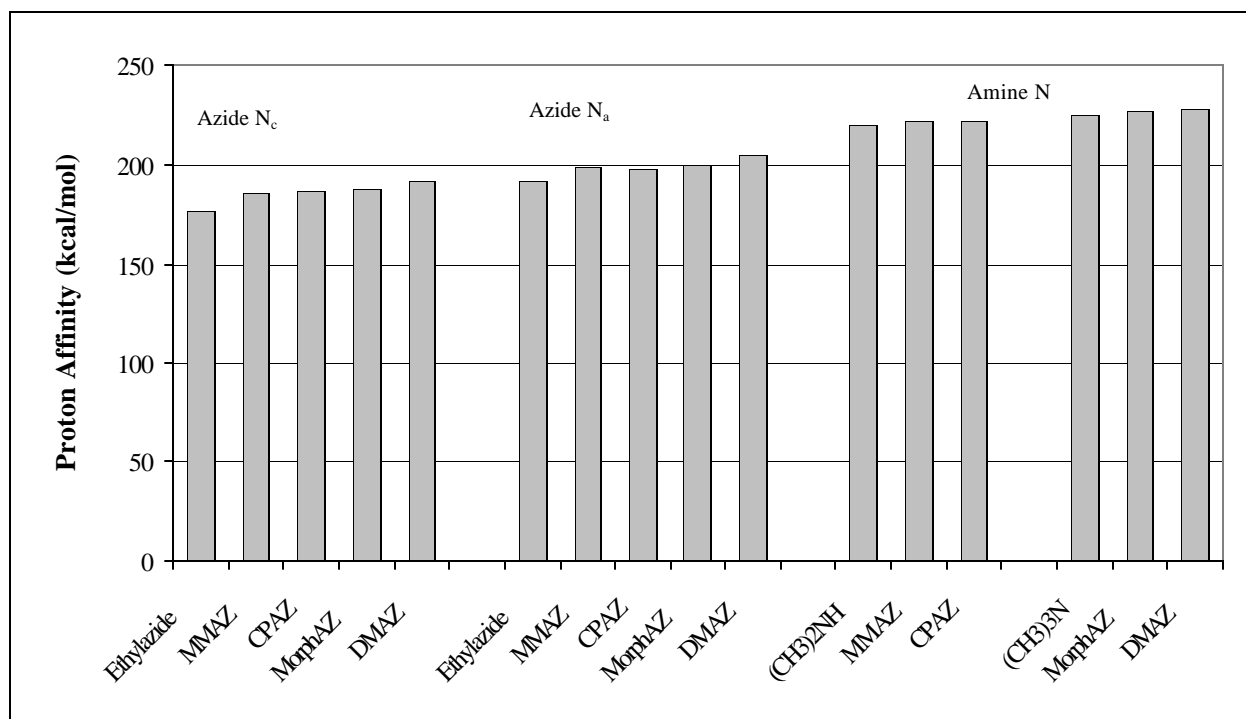
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Figure 8. B3LYP/6-311++G(d, p) calculated *PA*s for the lone pair sites of amine azide fuels. The *PA*s for the lone pair sites of ethylazide, dimethylamine, and trimethylamine are shown for comparison.

protonated ADMCPA structures upon which the *PA* calculations are based are also relatively high in energy. This would result in an underestimation of their value. A search for lower energy protonated structures for the ADMCPA isomers might address this issue, but given the lack of correlation between amine *PA* and ignition delay for compounds that have been synthesized and tested, the matter was not pursued for these notional ones.

The *PA*s of the lone pair sites associated with the bonding (N_a) nitrogen of the azide group in the amine azides all fall within a fairly narrow range that is ~10 kcal/mol higher than that of their "analogous" alkyl azide, (analogous meaning ethyl azide for molecules with ethyl azide chains and cyclopropyl azide for the ADMCPA isomers). However, the similarity of the increases observed in MMAZ, CPAZ, and DMAZ indicates that there is not a strong correlation between the *PA* of this site and ignition delay. Originally observed in DMAZ_B, where the amine and azide groups are in close proximity, it was thought that the increased *PA* was related to the direct interaction between the two groups. However, the effect is also observed in the D conformers of DMAZ, MMAZ, and CPAZ. Thus, it is assumed that the effect is passed through/from the ethyl chain connecting the groups.

The *PA*s of the terminal (N_c) nitrogen of the azido groups in MMAZ and DMAZ are also observed to be 10–15 kcal/mol higher than those of the analogous site in alkyl azides, and again,

12

the increase in DMAZ_B and DMAZ_D *PA*s are marginally higher than the *PA* increases found for their MMAZ analogs. The increases also appear to be independent of amine and azide group proximity. However, the increases in CPAZ and MORPHAZ are similar to those of MMAZ, denying a strong correlation between the *PA* of this site and ignition delay. The extremely high values observed for the ADMCPA isomers are related to the fact that the attachment of a proton at this site induces the cyclopropyl ring to break. Coupled with the indication that the increase in the *PA* of azide sites in 2-azidoethanamines is passed through/from the ethyl chain connecting the amine and azide groups, the possibility that the short ignition delay observed for DMAZ is related to a mechanism involving the ethyl chain is suggested and will be discussed in section 4.

Table 5 shows the *PA*s calculated for the lowest energy hydrazine, MMH, UDMH, and symmetric dimethylhydrazine (SDMH) structures. (Having a relatively high freezing point, SDMH is not a standard hypergolic fuel component.) The results are presented graphically in figure 9. The *PA*s for the hydrazine lone pair sites are, like amine sites, substituent dependent, increasing with the number of attached methyl groups. It is also observed that the *PA*s of the unmethylated nitrogens in the methylated hydrazines increase with the total number of methyl groups on the hydrazine. Finally, similarities in the *PA*s of the hydrazines and the amines (in table 1) are notable: (1) ammonia (204.0 kcal/mol) vs. hydrazine (204.2 kcal/mol), (2) methylamine (214.9 kcal/mol) vs. methylated nitrogen of MMH (213.3 kcal/mol), and (3) trimethylamine (226.8 kcal/mol) vs. the methylated nitrogen of UDMH (221.4 kcal/mol). These similarities are in contrast to the ignition delay differences observed for these compounds. Even within the hydrazine family, the *PA*-ignition delay correlation breaks down, MMH having an ignition delay equal to or shorter than UDMH, yet having a *PA* less than UDMH. Thus, a correlation between site-specific *PA*s and ignition delays does not appear to exist.

3.4 Fuel Cluster-Nitric Acid Complexation

Given that gas-phase reactions leading to separated ions are endothermic, questions about their relevance as a measure of an exothermic neutralization process can be raised. Therefore, the possibility that $\boldsymbol{DH_r(0)}$ values for ion pair formation reasonably estimate the heat of neutralization (and correlate with ignition delay) was considered. As an approach to this problem, the work of Tao (*13*) was initially followed. Characterizing the effect of water molecules on the interaction between ammonia and nitric acid in NH_3-HNO_3-$(H_2O)_x$ complexes, he showed that for complexes with as few as two water molecules, based on O-H_a and N-H_a bond distances, where H_a is the hydrogen atom originally associated with nitric acid, ammonia and nitric acid will exist as an ion pair—$(NH_4^+)(NO_3^-)$. In addition, Tao profiles the potential energy of the complex along a proton transfer reaction pathway (specified by fixing the O-H_a bond distance at values down to those approaching those in the unsolvated NH_3-HNO_3 complex) and interprets the results as a measure of the (energetic) stabilization provided by the stepwise addition of more water molecules. An intriguing approach because its results expose the
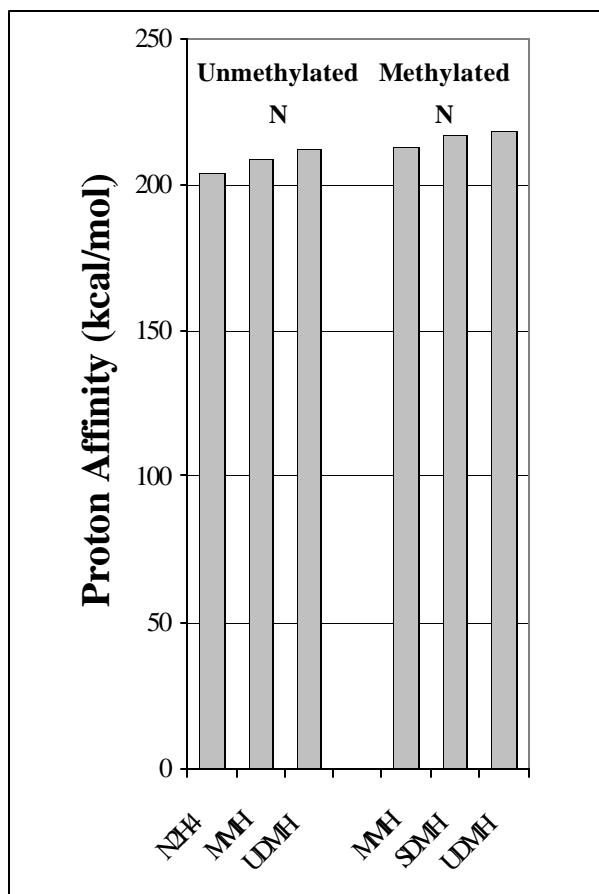
Figure 9. B3LYP/6-311++G(d, p) calculated *PA*s for
the lone pair sites of hydrazines.

competition between electrostatic attraction and the formation of more hydrogen bonds that drive proton transfer; analogous studies of $(NH_3)_x$-HNO_3 and $(N_2H_4)_x$-HNO_3 complexes were undertaken.

As shown in figures 10 and 11, on the basis of O-H_a and N-H_a bond distances, H_a is effectively transferred to the fuel molecule when the fuel-oxidizer interaction is mediated by two other fuel molecules. Figure 12 shows the increase in energy associated with reducing the O-H_a bond distance for the $(NH_3)_3$-HNO_3 and $(N_2H_4)_3$-HNO_3 systems. The results for the $(NH_3)_3$-HNO_3 system are very similar to those obtained by Tao for the NH_3-HNO_3-$(H_2O)_2$ system. The minimum energy is associated with an O-H_a bond distance of ~1.6 Å, and the energy increases ~4 kcal/mol when this bond distance is reduced to 1.0 Å. The results for the $(N_2H_4)_3$-HNO_3 system are similar to those of the $(NH_3)_3$-HNO_3 system, but the energy increase is slightly greater, a result one would expect for a fuel with a shorter ignition delay. Further consideration of the matter, however, raised questions about the validity of the comparison. For one, though each system has the same number of molecules, the system sizes are not the same.
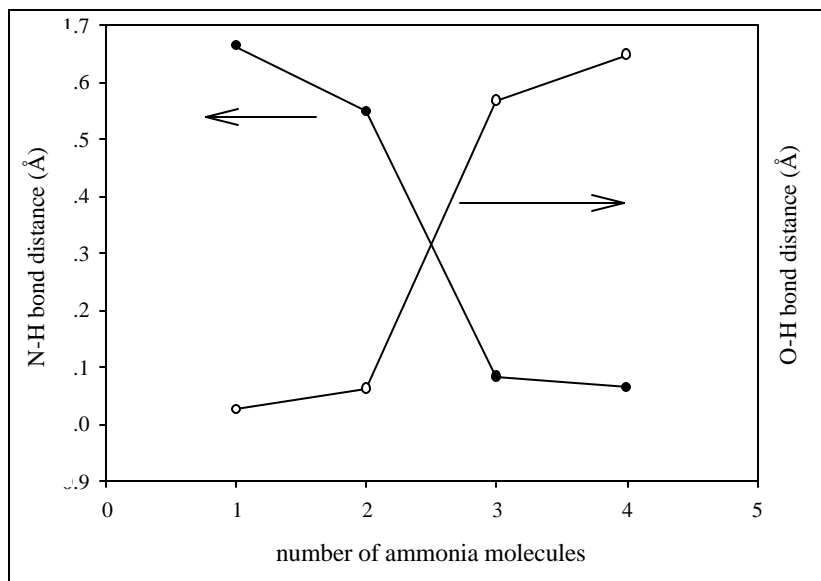
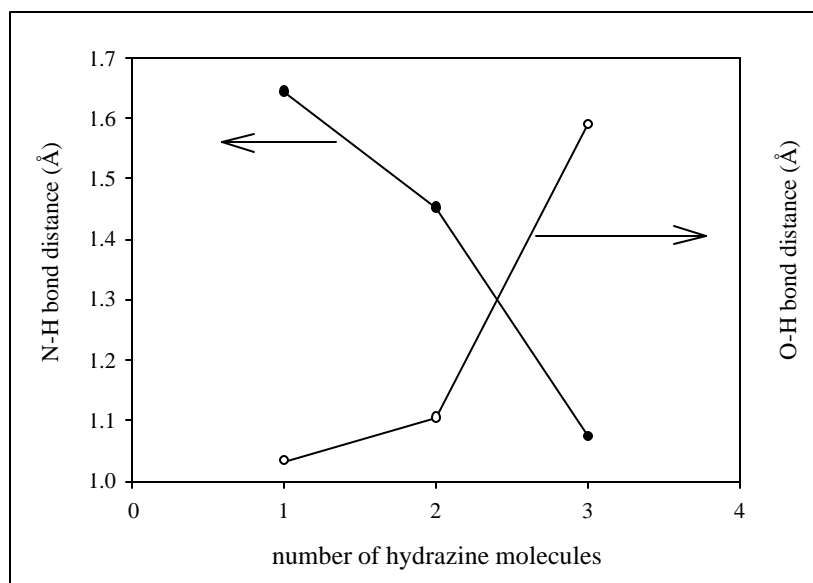Figure 10. O-H$_a$ and N-H$_a$ bond distances for (NH$_3$)$_x$-HNO$_3$ complexes.
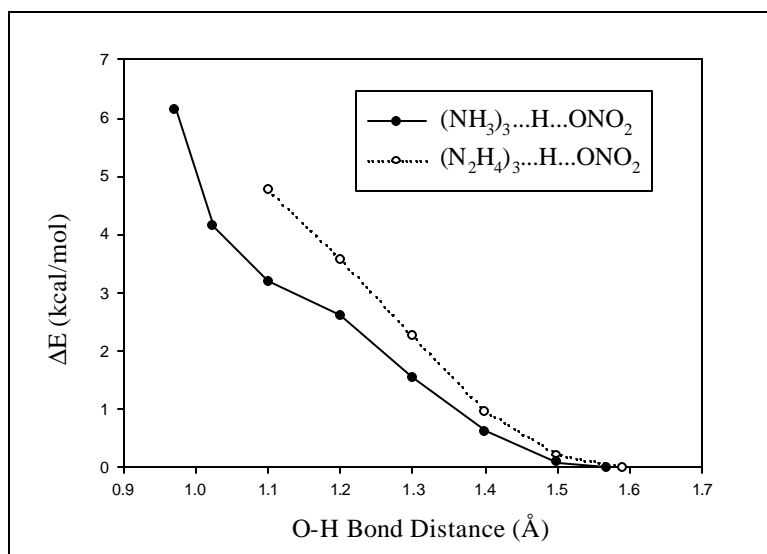

Figure 11. O-H$_a$ and N-H$_a$ bond distances for (N$_2$H$_4$)$_x$-HNO$_3$ complexes.

Figure 12. The energies of $(NH_3)_3$-HNO_3 and $(N_2H_4)_3$-HNO_3
complexes as a function of O-H_a bond distance.

The hydrazine system has three hydrazine-hydrazine hydrogen bonds while the ammonia system has only two ammonia-ammonia hydrogen bonds. This inequality could account for the observed differences.

Another potential problem with the approach has to do with the fact that the energy difference considered relevant is between the minimum energy structure and the energy of a structure with an O-H_a bond distance near 1.0 Å. But it is not clear that the latter distance (or any other) is optimum for the comparison. As shown in figure 12, the energy of the $(NH_3)_x$-HNO_3 complexes begins to increase rapidly as the O-H_a distance is reduced below 1.0 Å. This behavior is assumed to occur because forces associated with the repulsive inner wall of the oxygen atom's potential begin to dominate the interaction. Coupled with the system size issue, the author decided to abandon this computationally intensive method.

3.5   Binary Fuel-Nitric Acid Complexation

As a final method for measuring the base strength of a fuel, the exothermicity of fuel-nitric acid complexation,

$$B + HNO_3 \circledR B...HNO_3, \tag{9}$$

was calculated for many of the fuels considered previously. Provided in table 6 and shown graphically in figure 13, it is observed that there are some differences between the trends of this measure and the trends indicated by simple PAs. For example, in the case of the hydrazines though (consistent with base strengths based on gas-phase PAs) the bond strength at the methylated nitrogen is higher than the strength at the unmethylated nitrogen of the same molecule, the strength of the bonding at unmethylated nitrogen is inversely proportional to the total number of methyl groups on the molecule. The trends in bond strengths at amine sites do

Table 6. Exothermicity of fuel-nitric acid complexation.

Compound	DE (kcal/mol)	DH_v[a] (kcal/mol)	$DE+DH_v$ (kcal/mol)	Ignition Delays[b] (s)
Hydrazines				
Unmethylated N				
N_2H_4	−13.2	10.7	−2.5	—
MMH	−12.8	—	—	—
UDMH	−12.4	—	—	—
Methylated N				
MMH	−14.0	9.6	−4.4	—
UDMH	−14.5	8.4	−6.1	—
Amines				
NH_3	−12.4	4.8	−7.6	—
CH_3NH_2	−13.8	5.8	−8.0	∞
$CH_3CH_2NH_2$	−14.2	6.4	−7.8	2.03
$(CH_3)_2NH$	−14.6	6.0	−8.6	—
$CH_3CH_2CH_2NH_2$	−14.2	7.5	−6.7	1.73
$(CH_3)_2CHNH_2$	−13.9	6.8	−7.1	0.94
$(CH_3)_3N$	−14.5	5.2	−9.3	—
DMAZ	−11.1	—	—	—
Azides				
Terminal N				
Ethylazide	−4.8	—	—	—
DMAZ	−5.5	—	—	—
Bonded N				
Ethylazide	−8.0	—	—	—
DMAZ	−8.8	—	—	—

[a] DH_v values for hydrazines are from reference (*21*), while those for amines are as reported in Lange's Handbook of Chemistry, 15th Edition, J.A. Dean, ed.; McGraw-Hill Inc.: New York, 1999.
[b] Reported in reference (*4*).

not track *PA* results either, indeed seeming to correlate better with pK_a results. Table 6 includes amine ignition delay results reported by Rapp and Streier (*4*). No correlation with $DH_r(0)$ values is observed. Even with differences in DH_v taken into consideration, the expected correlation does not emerge. The $DH_r(0)$ values for the two azide lone pair sites do follow *PA* results, but the differences are not as compelling. Therefore, investigations along this line were terminated.

4. Discussion

Despite the expectation that ("all else being equal") a stronger base will have a shorter ignition delay, such a correlation was not observed. In retrospect, the information already available for hydrazine and its derivatives presaged the lack of correlation. As measured through their
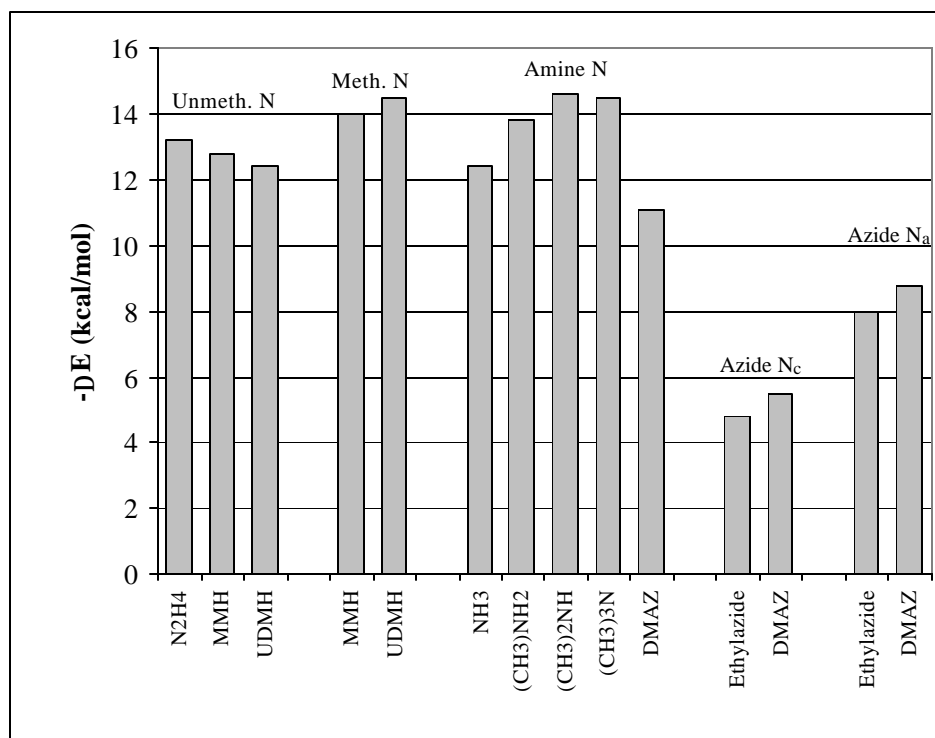
Figure 13. Heats of complexation for fuel-nitric acid complexes.

titration with hydrochloric acid in an aqueous solution, the pK_a and heat of neutralization of MMH are lower than those of hydrazine. Moreover, MMH has a lower dielectric constant than hydrazine, so the differences in reaction (5) heats of neutralization should be even larger than indicated by the aqueous-phase results. But in all RFNA-oxidized studies of which the author is aware, MMH yields shorter ignition delays.

In the case of amines, the work by Rapp and Strier (*4*) seems to support a correlation between fuel basicity and ignition delay, but Schalla and Fletcher's (*6*) results clearly point to the correlation's shortcomings as a predictive tool. Looking at variations in ignition delay as a function of a number of variables, including (1) O/F ratio, (2) bomb volume, (3) volume of propellant charge, (4) gas-phase oxygen concentration, and (5) water content, these researchers did find that the shortest ignition delays for a triethylamine-WFNA system were for a fuel mole fraction near 0.41 (O/F = 1.4), a value that is closer to stoichiometric for neutralization (i.e., O/F = 1.0) than stoichiometric for combustion (O/F ~ 8). (However, it is only on either side of these limits that the delays get really long.) Indicating the importance of neutralization, these researchers nonetheless sought to rationalize why neutralization stoichiometry did not yield the shortest delays (though they should produce the largest liquid-phase temperature rises). They postulate that the mixture needs to be somewhat lean in order to produce/have available gas-phase oxidizers. (If all the oxidizer goes towards neutralizing the amine, none are left for gas phase oxidation.) The shortest ignition delays observed in their study were for systems that were

stoichiometric with respect to neutralization and had gas phase oxidizers (O_2 and NO_2) already available in the initial atmosphere.

As a final note, Schalla and Fletcher (*5, 6*) speculate that the best amine-acid propellant combinations would be those whose stoichiometries for both neutralization-nitration and fast-efficient combustion are about the same, the case for (at that time standard) propellant combinations like hydrazine-WFNA and aniline-WFNA. In view of this speculation, it is interesting to consider the O/F ratios that optimize DMAZ, MMAZ, and CPAZ performance. Based on National Aeronautics and Space Administration (NASA)-Lewis thermochemical code calculations presented elsewhere (*19*), O(IRFNA)/F ratios that optimize the impulse of DMAZ, MMAZ, and CPAZ are 2.4, 2.4, and 2.6, respectively. In the case of MMH with IRFNA, the value is also 2.6. Thus, even with this added consideration, the nonhypergolicity of MMAZ is not explainable.

Despite the failure of the computed measures of base strength to correlate with ignition delays, the study suggests an alternate explanation for the relatively short ignition delays observed for 2-azidoethamines compared to alkyl amines or alkyl azides. The relatively high *PA*s of the lone pair sites of azide groups in 2-azidoethamines and the fact that the effect is passed from/through the chain linking the amine and azide groups indicate that bond cleavage or H-atom abstraction from the chain might be facilitated. Such mechanisms might also explain the difference in performance of MMAZ and CPAZ. To investigate this possibility, a study to characterize (gas-phase) reactions of MMAZ, CPAZ, and DMAZ is planned.

5. Summary

Various approaches to the computation of basicity have been applied in an attempt to characterize this property for hypergolic fuels with measured ignition delays. The CPCM as implemented in the G98 suite of QM codes produces condensed-phase heats of neutralization for amine and hydrazine compounds reacting with nitric acid that are questionable. The energetics of proton transfer from nitric acid to small (gas-phase) fuel clusters appear to be reasonably calculated via density functional theory methods, but even for the largest clusters considered tractable, the neutralizations are endothermic, raising concerns about their relevance as a measure of the exothermic condensed-phase process of interest. Gas-phase *PA*s, which are relatively simple to calculate, identify substituent-dependent differences in the basicity of lone pair sites, but correlations with ignition delay were not observed for the 2-azidoethanamines considered. Differences between the *PA*s of azide lone pair sites in alkyl azides and analogous amine azides are striking, but a correlation with ignition delay was not observed. The study does suggest the possibility that reactions involving the ethyl chain connecting the amine and azide groups are responsible for the unexpectedly short ignition delays observed in 2-azidoethanamine-fueled systems.

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22

ABERDEEN PROVING GROUND

28   DIR USARL
      AMSRD ARL WM BD
       W R ANDERSON
       R A BEYER
       A L BRANT
       S W BUNTE
       C F CHABALOWSKI
       L M CHANG
       T P COFFEE
       J COLBURN
       P J CONROY
       R A FIFER
       B E FORCH
       B E HOMAN
       S L HOWARD
       P J KASTE
       A J KOTLAR
       C LEVERITT
       K L MCNESBY
       M MCQUAID
       M S MILLER
       A W MIZIOLEK
       J B MORRIS
       J A NEWBERRY
       M J NUSCA
       R A PESCE-RODRIGUEZ
       G P REEVES
       B M RICE
       R C SAUSA
       A W WILLIAMS

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